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Tunable defect modes in chiral liquid crystals based on laser-induced modulation of helix

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ABSTRACT

A structural defect was introduced within the helical lattice of cholesteric liquid crystals to realize a tunable photonic defect mode in the selective reflection band, or the polarization sensitive photonic band-gap of the cholesteric liquid crystal. The cholesteric liquid crystal material was locally polymerized via a two-photon polymerization process and a finite unpolymerized region was left between two polymerized layers to act as the structural defect in which the helical pitch is different from the polymerized bulk. The structural defect was functionalized by first of all, rinsing the unpolymerized cholesteric liquid crystal, and then infiltrating a photo-chromic dye-doped cholesteric liquid crystal material into the gap. A defect mode was observed in the selective reflection band of the cholesteric liquid crystal material at a wavelength depending on the contrast between the pitch at the defect and the bulk. The defect mode was tunable by applying heat or irradiating light at $\lambda \sim 400$ nm on the sample, which caused the shortening of the helix pitch of the cholesteric liquid crystal at the defect, therefore increasing the pitch contrast between the bulk and the defect. Reversible tuning of the defect mode was realized in an electrode-free cell.

Keywords: Cholesteric liquid crystals, photonic crystals, defect mode, photo-chromism

1. INTRODUCTION

Photonic crystals (PhCs) are periodic dielectric media with fascinating potential to enable the control of photons. They exhibit what are called photonic band-gaps (PBGs) in which light transmission is prohibited over a wavelength range given by the refractive index and the periodicity of the structure^{1,2}. While a defect-free PhC can act as a perfect mirror, a structural defect in the periodic lattice causes light to be confined both spatially and spectrally at the defect and a "defect-mode" is permitted within the PBG. Exploitation of this property adds a range of functions and applications for PhCs, which some include narrow band-pass filters³, low threshold lasers⁴ and optical add and drop⁵. Further functionalization of PhCs have been attempted in structures incorporating functional materials into the periodic lattice; functional indicating that they change their physical properties such as their refractive index by an external triggering signal. They have opened a new and exciting topic in the field of PhCs called tunable PhCs, in which the optical properties can be tuned to meet certain specifications by external fields⁶⁻¹⁰.

While many PhCs with one, two or three-dimensional (1, 2, 3-D) periodicities have been fabricated and investigated using conventional semiconductor processing methods such as electron-beam lithography, nature also displays a fascinating range of photonic crystals, in which periodic structures are formed spontaneously. Microscopic pores were known to exist in peacock feathers and in the wings of certain morph butterflies, giving them radiant colors from multiple reflections. Opals are an example of a more well-defined 3-D PhC, in which spheres with several hundred nanometer diameters self-assemble into a face-centered-cubic configuration. The exploitation of these self-organizing periodic structures for the preparation of PhCs for particular applications would be an intelligent, less time-consuming alternative to conventional methods, should the structures be controlled to a certain degree that desirable characteristics are achieved.

Cholesteric liquid crystals (ChLCs) with chiral constituents are 1-D self-organizing PhCs with great potential due to their extremely easy preparation process and tunability. The chiral constituents doped in a conventional nematic LC host cause the molecules to self-organize into a helical periodic structure with a periodicity called the pitch, which can range from few 100 nms to several mms, depending on the type and concentration of the material. Owing to the helical structure, they exhibit a 100% selective reflection for circularly polarized light with the same circular handedness as the material, in the wavelength region described by $\lambda = n_o p \sim n_e p$, where n_o and n_e are the ordinary and extraordinary

refractive indices, and p is the pitch¹¹. Tunability in ChLCs is realized by utilizing the external field sensitivity of the LC molecules or by doping certain functional molecules to induce a change in the refractive indices or the pitch. Thermal control the ChLC pitch¹² or a fabrication of a spatial modulation of the ChLC pitch^{13,14} are some examples, while on the other hand, the helix can be stabilized by polymerizing the material in ChLCs with doped photo-reactive monomers¹⁵. Optical tuning of the PBG has also been demonstrated in azobenzene dye-doped ChLCs, which exhibit a trans-cis isomerization upon UV exposure and affect the helical pitch¹⁶⁻¹⁹. Photo-tuning of the PBG is useful especially because reversible tuning is realized in electrode-free cells.

In this study, structural defects are fabricated into the helical lattice of the ChLC in an aim to realize a PhC with tunable defect-mode by a simple and non-time consuming fabrication process. Considerable amounts of theoretical and experimental work have been conducted on the defect modes exhibited in ChLCs: from introducing a simple isotropic defect layer²⁰ to a introducing a nematic LC defect²¹ or even a twisted phase shift^{22,23} in the LC director, however the defect medium suitable for the realization of a tunable photonic defect-mode and the configuration which will be investigated in this study is a ChLC material with a different pitch from the bulk²⁴. The defect mode wavelength is determined by the contrast in the pitch length at the bulk and the defect, which allows tuning of the defect mode if selective pitch modulation can be induced either at the defect or the bulk. The authors introduce the defect by a direct-laser scanning method where a polymer-LC hybrid structure is fabricated by locally polymerizing the material²⁵. The structure is further functionalized by inserting a azobenzene dye-doped ChLC material in the defect, to realize optical tuning of the photonic defect mode by selective pitch modulation of the defect. The experimental methods for the preparation of the sample will first be presented, followed by an investigation of the tuning properties of the photonic defect mode.

2. EXPERIMENTAL

2.1 Fabrication of a structural defect in ChLCs by the direct laser lithography method

A schematic of the fabrication process of a defect within ChLCs is shown in Fig. 1. 100-fs pulses from a Ti:Sapphire laser [Spectra Physics: Maitai] operating at $\lambda = 800$ nm and 82MHz were focused within the cell by a high-NA (1.4) lens and scanned over a rectangular area of approximately $146 \times 146 \mu\text{m}$. Two-photon absorption corresponding to light at $\lambda \sim 400$ nm is induced in the vicinity of the laser focus, and a finite polymerized region is formed. The two-photon polymerization (TPP) process is performed on both sides of the sample substrate, so that a finite unpolymerized region is left between two polymerized regions, to act as the defect layer. Fabrication was conducted at 40°C by placing the sample on a hotplate, placed on a confocal laser-scanning microscope [Zeiss: LSM-510] setup. The thickness of the polymerized ChLC was measured in-situ by confocal laser-scanning fluorescence microscopy, and also by a scanning electron microscope.

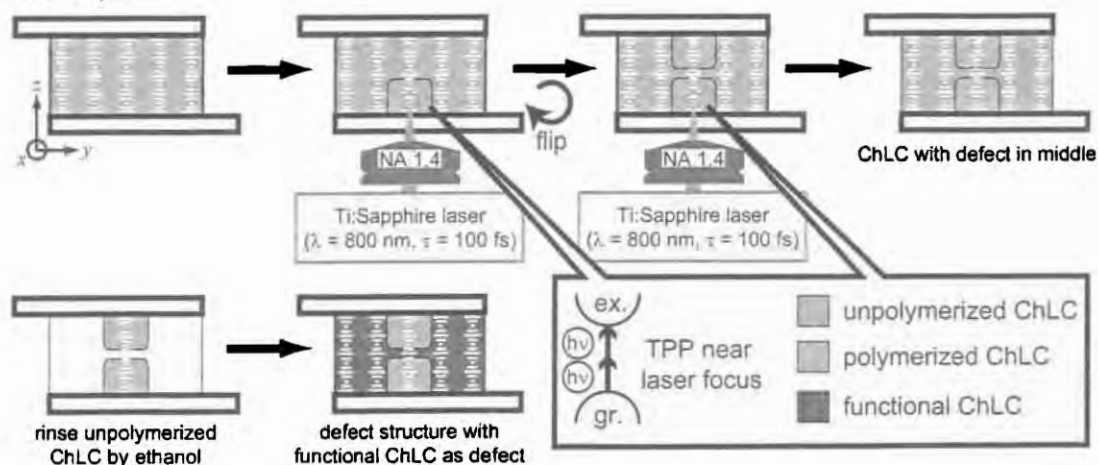


Fig. 1. A schematic of the fabrication process of the ChLC defect structure considered in this study.

After the fabrication of the ChLC structure, the unpolymerized ChLC was rinsed out of the cell by immersing the sample in ethanol. Only the ChLC monomer was rinsed out by this process, since the polymerized region remains intact with the cell substrate. An azobenzene dye-doped ChLC material was then infiltrated in the sample to realize a ChLC defect structure with a photo-functional defect.

2.2 Sample

The photo-polymerizable ChLC material used in this study was prepared by Merck KGaA to have a right-handed helix with the central wavelength of the selective reflection band appearing at $\lambda_s \sim 570$ nm and possessing a cholesteric – isotropic transition temperature of $T_{iso} \sim 76.0^\circ\text{C}$. The material shows no absorption at $\lambda \sim 800$ nm while polymerizing at 400 nm, which makes them an ideal material for processing by the direct laser lithography method. The photo-polymerizable ChLC was infiltrated in a sandwich cell made from two cover slips with an approximate spacing of 5.5 μm , rubbed to obtain a planar alignment with the helical axis perpendicular to the substrates. The mixture also included 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran [Excitation: DCM] dye by 0.6 wt% for observation purposes on the confocal laser-scanning microscope.

As the template ChLC material, a photo-chromic, right-handed ChLC was prepared by mixing a chiral dopant [Merck: R-811] into a nematic LC host [Merck: E-44] by 30 wt%, and adding azobenzene-dye [Tokyo Chemical Industry: 4-diethylaminoazobenzene] by 3.8 wt%. The azobenzene dye-doped ChLC is known to exhibit pitch-shortening upon irradiation of light with a certain wavelength owing to the increase in the chirality caused by the trans-cis isomerization of the dye. The molecular structure of the azobenzene dye used in this study is shown in Fig. 2.

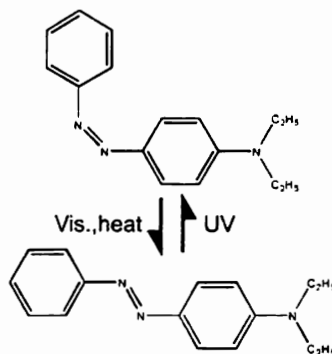


Fig. 2. Molecular structure of 4-diethylaminoazobenzene and its photo-isomeric states.

2.3 Measurements of the optical properties

The thermal-tuning properties and the optical-tuning properties of the fabricated structure were investigated by measuring the transmittance spectrum on a microscope [Nikon: Optiphot 2] over a spot of radius $\phi \sim 20$ μm (using an objective with NA 0.5) by a CCD multichannel spectrometer [Hamamatsu Photonics: PMA-11] with a spectral resolution of ~ 2 nm. The polarization of the incident wave was changed between linear and circular polarization by inserting a $\lambda/4$ plate. The thermal-tuning properties were investigated for temperatures between 20.0°C to 60.0°C by controlling the sample temperature on a hotplate. The optical tuning characteristics of the transmittance spectrum was measured upon coaxially irradiating the sample by a high-pressure mercury lamp [Nikon: HB10101AF] with power ~ 17 mW/cm^2 . The reversibility of the tuning properties was investigated by performing a 40 second cycle in which the UV light was irradiated for 15 seconds and then cut-off for 25 seconds for 5 minutes.

3. RESULTS AND DISCUSSION

3.1 Local polymerization of the ChLC by direct laser lithography

The thickness of the ChLC material being polymerized by the two-photon absorption process can be controlled by the laser-scanning conditions. Figure 3 shows the thickness of the polymerized region obtained at various laser-scanning conditions. The results show that the thickness of the polymerized ChLC is proportional to the intensity of the laser and the scan-speed of the laser. The thickness is controlled with a vertical resolution of approximately 200 nm, although it may become smaller upon optimizing the materials or the laser irradiation conditions. They thus allow structural defects that are small enough to exhibit single modes to be introduced, which is often difficult to obtain by the polymer-ChLC stacking process, which is a mechanical process²¹. Optical measurements were conducted on a sample with two polymerized regions formed at a laser intensity of 3.16 MW/cm^2 and laser scan-speed of $126 \mu\text{s}/\mu\text{m}^2$, which gives an approximate thickness of $2.1 \mu\text{m}$. The confocal laser-scanning fluorescence micrograph and the height profile of the ChLC with the rectangular polymerized region are shown in Fig. 3 (b), which indicates that a defect with approximate thickness of $0.87 \mu\text{m}$ is fabricated.

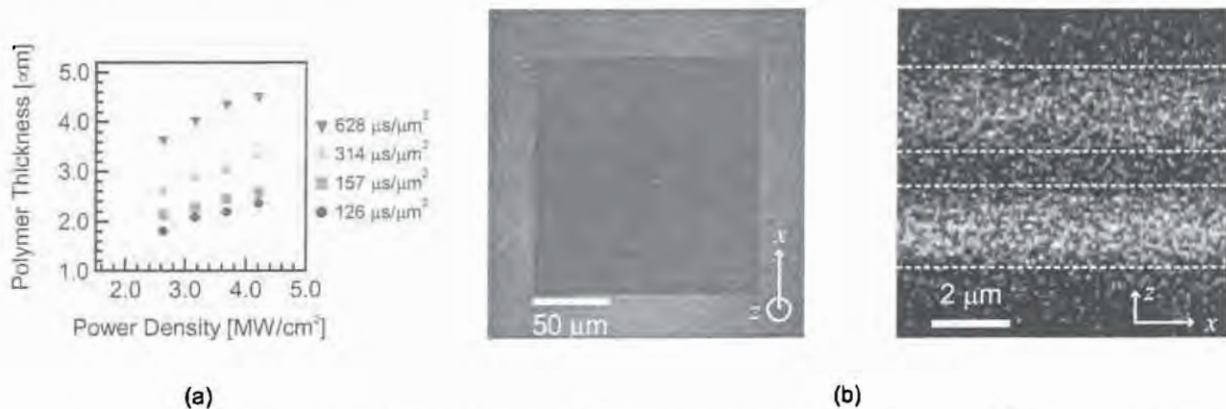


Fig. 3. (a) Approximate heights of the polymerized ChLC structures upon laser irradiation at different scan-speeds and intensities, measured on a SEM. (b) An example of an in-situ observation of the fabrication process, where the darker rectangular region indicates the polymerized ChLC region (left), and the depth-wise fluorescence profile of the fabricated structure, which gives an estimate of the bulk regions and the defect regions (right).

3.2 Optical properties of the ChLC defect structure

Figure 4 shows the transmittance of spectrum of the fabricated structure upon incidence of right and left circular polarized light, at $T = 30^\circ\text{C}$. Within the PBG exhibited between $564 - 657 \text{ nm}$, a sharp peak corresponding to the defect mode is observed at 632 nm , which confirms the introduction of a defect in the ChLC. It is particularly interesting, however, that selective reflection is exhibited by the fabricated structure, even at the defect mode wavelength. This is contrary to certain kinds of defect media such as isotropic media¹⁹ or a cholesteric phase twist^{21,22} where light with the circular polarization in the direction opposite to that of the medium is also affected.

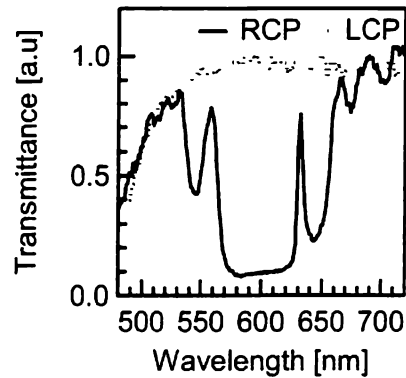


Fig. 4. Incident polarization dependence of the transmittance spectrum of the ChLC defect structure.

3.2.1 Thermal tuning of the defect mode

Figure 5 shows the temperature dependence of the PBG of the azobenzene dye-doped ChLC material. The transition temperature from ChLC to isotropic phase is approximately at 57°C, and a blue-shift of the PBG corresponding to pitch shortening is observed upon increasing the temperature, until the liquid crystallinity starts to decrease at 52°C and the PBG becomes narrower. The stepwise shift of the PBG corresponds to a discrete change in the number of half-pitches in the cell, due to the strong anchoring of the molecules at the substrate surface, rubbed to align the molecules in a planar orientation.

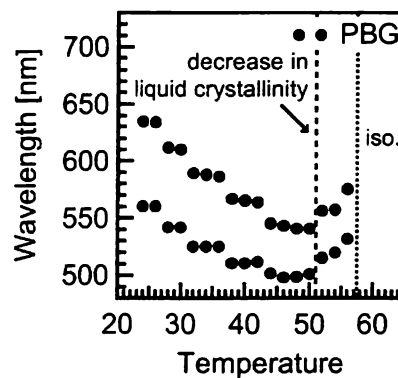


Fig. 5. The temperature dependence of the PBG of the azobenzene dye-doped ChLC.

Figure 6 shows the transmittance spectrum of the fabricated structure upon right circularly polarized light incidence. As the temperature of the sample is increased, a blue-shift of the photonic defect mode is exhibited. The direction of shift matches that of the azobenzene dye-doped ChLC introduced in the defect, and is also consistent with theoretical results in the literature that, when the pitch of the defect is shorter than in the bulk, the defect mode shows a blue-shift with increasing contrast in pitch (and vice versa)²⁴. It should be noted that the contrast of the pitch lengths between the bulk and the defect is increased in this specific configuration with two polymerized ChLC regions sandwiching the defect layer: the ChLC at the defect is selectively pitch-shortened since the polymerized region becomes highly thermally stable and does not change the pitch upon heating. Although the observations can be explained qualitatively, certain quantitative issues remain unanswered, such as the continuous shift exhibited by the defect mode, contrary to that exhibited in a conventional LC. One possible explanation may be that LC director distribution is distorted from the ideal sinusoidal distribution; however, further investigation is required to confirm this model. The discrete shift observed at 58°C, on the other hand, corresponded to phase transition where the helical structure disappeared and the medium became isotropic. The defect-mode tuning over a bandwidth of approximately 42 nm was reversible, with no decline in the transmittance spectrum after several repetitive measurements.

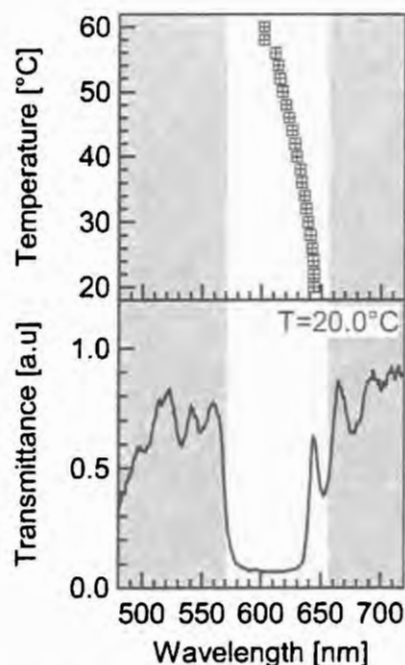


Fig. 6. The transmittance spectrum of the ChLC defect structure and its thermo-tuning properties, measured upon right circularly polarized light incidence.

3.3 Optical tuning of the defect mode

The time dependence of the spectral position of the PBG of the azo-ChLC upon light irradiation is shown in Fig. 7 (at 30°C). A reversible shift of the PBG was observed, with a blue-shift upon light irradiation, and an opposite red-shift after removing the light source. The blue-shift corresponded to the pitch-shortening of the ChLC caused by the trans-cis isomerization of the azobenzene dye inducing an increase in the helical twisting power of the ChLC. Both forward (reaching an equilibrium state after ~ 6 seconds) and reverse (caused by a relaxation to the thermally preferred trans state over a timespan of ~30 seconds) reactions commenced at the initiation and termination of light exposure, and a small domain with a shorter or longer pitch gradually grew throughout the sample. The transmittance spectra changed in a step-wise manner as the domain grew over the measurement spot. The step-wise shift of the PBG corresponds to the discrete winding of the ChLC helix, caused by the strong anchoring at the substrate surfaces.

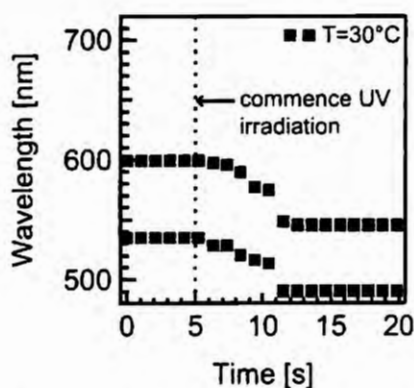


Fig. 7. Shift in the PBG of the azobenzene dye-doped ChLC upon light irradiation at $\lambda \sim 400$ nm and $P \sim 17$ mW/cm².

Figure 8 shows the transmittance spectrum of the defect mode exhibited by the fabricated structure upon light irradiation (at 30°C). The defect-mode blue-shifted upon irradiation, corresponding to an increase in the pitch contrast between the defect and the bulk, due to the selective pitch-shortening of the azo-ChLC at the defect while the polymerized ChLC in the bulk remains unaffected. A time-resolved measurement of the defect-mode wavelength (Fig. 8 (b)) indicated that the defect-mode exhibited initially at $\lambda \sim 632$ nm shifts to $\lambda \sim 620$ nm within 4 seconds of light irradiation, and returns to its original wavelength approximately after 10 seconds of light termination. The dynamic response curve revealed two components working in the system: a gradual shift observed from initiation to approximately after 3 seconds of light irradiation, and a larger, discrete shift observed at approximately 4 seconds. There may be a weaker anchoring effect of the polymer, or a distribution of the pitch within the defect in play to cause this observation: a gradual shortening of the ChLC pitch may be permitted by the weaker anchoring until a discrete shift becomes energetically preferable. The smaller number of discrete winding (and the corresponding shift) compared to the case when light was irradiated on the azo-ChLC in a conventional cell may be attributed to the less amount of light reaching the azo-ChLC at the defect, because of the absorbance of the DCM dye in the polymerized ChLC. The system exhibited good reversibility over the course of the experiment and the transmittance of the defect mode did not show any decline even after repetitive light irradiation.

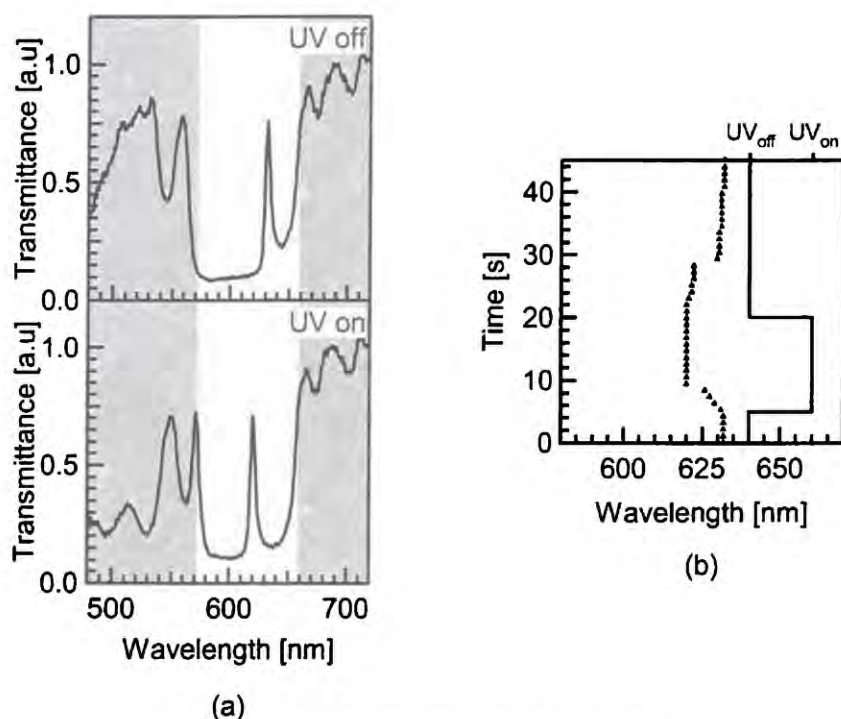


Fig. 8. (a) The transmittance spectrum of the fabricated structure before and after light irradiation (at $T = 30^\circ\text{C}$), and (b) the dynamic response of the defect-mode wavelength.

4. CONCLUSIONS

Tunable photonic defect-modes in ChLCs has been demonstrated by inducing a local polymerization of the helix by a two-photon absorption process, after which an azobenzene dye-doped ChLC material was introduced to act as the defect medium. The defect mode wavelength was dependent on the contrast in the pitch length between the bulk and defect, and a tuning of the defect mode wavelength was demonstrated by selectively inducing a pitch-shortening of the defect by either thermal effects or light irradiation. Preliminary results on reversible and reproducible tuning of the defect mode were presented, although further optimization of the structure and the materials, as well as investigations of the LC director distribution within the system would be vital to exploit these structures and to achieve faster and wider tuning.

characteristics. Electrode-free, intelligent optical components may be realized after sufficient optimization of these structures.

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